Art. XIII.—*On the Synthesis of Sugar from Formaldehyde and its Polymers, its Quantitative Relations and its Exothermic Character.*

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In 1861 Butlerow found that on treating trioxymethylene trimolecular formaldehyde) with hot lime water, a sweet yellow, unfermentable syrup, "methylenitan," was obtained. Loeb[1] obtained an unfermentable " formose " syrup by the prolonged action of lime water on dilute formaldehyde, and by using magnesia obtained a " methose " syrup containing fermentable sugar. Fischer[2] showed that all three syrups were complex mixtures, containing a acrose and obtained this sugar, and β acrose from Barium hydrate and aerolein bromide. The a acrose is optically inactive fructose, and the β acrose is inactive sorbose.

The methods used for the preparation of sugar are mostly slow ones, involving incomplete reactions, and no attempts appear to have been made to determine any precise quantitative relations of the reacting materials.

In a previous paper[3] a method was described of rapidly polymerising formaldehyde to sugar by running dilute caustic soda into a boiling weak solution of formaldehyde, containing calcium formate. The advantages of this method are that there is a definite end reaction, so that quantitative estimations are possible, that the process is very rapid, requiring only a few minutes for completion, and that the amount of formaldehyde polymerised is very large. The residual products are calcium and sodium formates, and sugars, mainly pentoses and hexoses, any methyl alcohol formed boiling off.

At low temperatures the reaction is extremely slow, and but little sugar is formed, while when strong caustic soda (35-40%) is

1. Loeb, Ber. D. Chem. Ges. 1887, Vol. 20, 142, 3039; 1888, Vol. 21, 270 ; 1889, Vol. 22, p. 470.
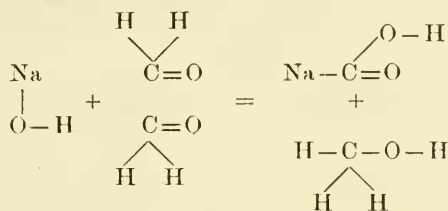2. Fisher, Ber. d. Chem. Ges. 1894, seq.
3. Ewart, Proc. Roy. Soc. of Vict., 1919, Vol. XXXI., p. 379.

boiled with concentrated formaldehyde mainly sodium formate and methyl alcohol are produced.
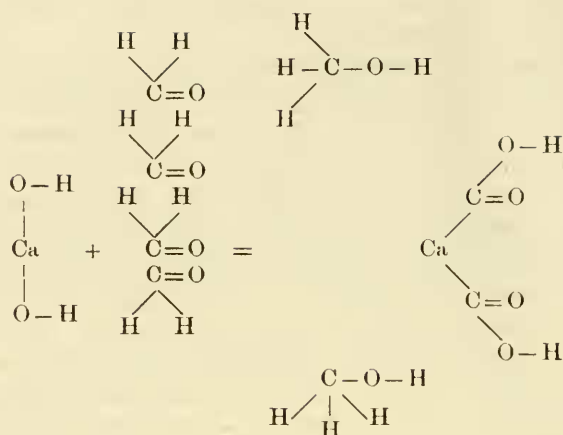
The purpose of the following investigation was to determine more closely the conditions determining the reaction, and bringing about the maximum polymerisation. The nature of the reaction appears to be as follows :—The sodium hydrate first reacts with the calcium formate, producing calcium hydrate, and sodium formate. The calcium hydrate has a more energetic polymerising action than sodium hydrate, and as this action takes place, it is converted into calcium formate, and methyl alcohol is produced. The amount of free alkali present at any given moment is, therefore, small in proportion to the amount of formaldehyde. If any free caustic alkali is present the sugar produced is caramelised on boiling, and the liquid turns brown. A drop or two of free alkali added in excess produces this change at the end of the reaction.

The polymerising action of an alkali appears to depend partly upon its valency. Thus the divalent Mg, Ca, Sr and Ba, hydrates appear to produce more polymerisation than the monovalent Na. and K, hydrates, the relative order being Ca, Sr, Ba, Mg, K, Na. Hence in the presence of a calcium salt, much more polymerisation takes place than if sodium hydrate is added directly to the boiling formaldehyde solution. We might picture the reaction with formaldehyde when no polymerisation takes place as follows :—

$$
\begin{array}{ccc}
 & \text{H} \quad \text{H} & \\
 & \diagdown\diagup & \text{O}-\text{H} \\
\text{Na} & \text{C}=\text{O} & \diagup \\
| & \quad + \quad = & \text{Na}-\text{C}=\text{O} \\
\text{O}-\text{H} & \text{C}=\text{O} & + \\
 & \diagup\diagdown & \text{H}-\text{C}-\text{O}-\text{H} \\
 & \text{H} \quad \text{H} & \diagup\diagdown \\
 & & \text{H} \quad \text{H}
\end{array}
$$

The sodium displaces hydrogen in the first CH_2O molecule, which together with the HO radicle of the sodium hydrate, displaces oxygen from the 2nd molecule. This is transferred to the first one, producing sodium formate and leaving methyl alcohol.

With calcium hydrate the reaction would take place similarly, but with four molecules of formaldehyde.

$$
\begin{array}{c}
\mathrm{O-H} \\
\mid \\
\mathrm{Ca} \\
\mid \\
\mathrm{O-H}
\end{array}
\;+\;
\begin{array}{c}
\mathrm{H\ \ H} \\
\diagdown\diagup \\
\mathrm{C=O} \\
\mathrm{H\ \ H} \\
\diagdown\diagup \\
\mathrm{C=O} \\
\mathrm{H\ \ H} \\
\diagdown\diagup \\
\mathrm{C=O} \\
\mathrm{C=O} \\
\diagup\diagdown \\
\mathrm{H\ \ \ H}
\end{array}
\;=\;
\begin{array}{c}
\mathrm{H} \\
\diagdown \\
\mathrm{H-C-O-H} \\
\diagup \\
\mathrm{H} \\
\\
\mathrm{O-H} \\
\diagup \\
\mathrm{C=O} \\
\diagup \\
\mathrm{Ca} \\
\diagdown \\
\mathrm{C=O} \\
\diagdown \\
\mathrm{O-H} \\
\\
\mathrm{C-O-H} \\
\diagup\ \mid\ \diagdown \\
\mathrm{H}\quad\mathrm{H}\quad\mathrm{H}
\end{array}
$$

It is not easy at first to see why under any conditions this reaction should lead to a production of sugar, nor would it in all probability if it were a simple matter of a reaction between formaldehyde and an alkali. Bearing in mind the fact that when a previously measured quantity of dilute alkali is run into boiling dilute formaldehyde, the reaction is completed, and sugar is produced within two or three minutes, or even more rapidly if an excess of soda is used, whereas the same solutions kept at 12 to 15°C. for two months or more develop little or no sugar, it seems probable that this difference can hardly be due wholly to the influence of temperature on the rate of chemical reaction.

If a strong solution of formaldehyde is boiled down to $\frac{1}{5}$ or $\frac{1}{6}$ its bulk, and cooled, it solidifies to a white waxy mass of the polyhydrate of formaldehyde. None appears while the liquid is boiling, because of its low melting point. When a litre of 1 or of 2% formaldehyde is boiled nearly to dryness, and then cooled, it leaves a considerable solid residue of the polyhydrate of formaldehyde. Hence, in spite of the loss of formaldehyde vapour, a dilute solution can be concentrated by boiling. If the solution is evaporated at a lower temperature, or under reduced pressure all, or nearly all the formaldehyde escapes, and no residue is left. Presumably therefore, in boiling water, the substance exists mainly as the polydrate of formaldehyde, or as paraformaldehyde, which, on cooling, partially dissolves and partially dissociates to formaldehyde, so long as it has not separated out in mass. Hot water poured into paraformaldehyde or the solid polyhydrate soon acquires a smell of

CH_2O, and the solid slowly disappears in excess of hot water. In cold water a large part is still present, undissociated, after three days.

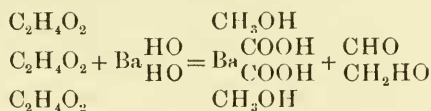Paraformaldehyde, or the polyhydrate, dissolves in a few hours in excess of cold 2% NaHO, the liquid smelling of CH_2O, but also containing a little sugar. In cold, strong 35% NaHO, solid paraformaldehyde at once dissolves, forming a yellow liquid smelling of CH_2O, and containing sugar. It blackens and gives a caramel smell, with sulphuric acid, gives Molisch's test (a naphthol) for carbohydrates, and yields furfural on boiling with hydrochloric acid.

Hence, paraformaldehyde and the polyhydrate yield sugar immediately in contact with cold, concentrated soda, whereas formaldehyde does not.

If hot, 35% NaHO is added in slight excess to melted paraformaldehyde, there is a sudden evolution of methyl alcohol, and the resulting brown liquid contains sodium formate and reducing sugar.

Hence it may be concluded that in boiling water the formaldehyde exists mainly as paraformaldehyde or the polyhydrate, and that the alkali produces sugar, methyl alcohol and sodium formate, when it reacts with paraformaldehyde or the polyhydrate, but only or mainly sodium formate and methyl alcohol when it reacts directly with formaldehyde.

Suppose three molecules of di-molecular formaldehyde react with one of Barium or calcium hydrate, as follows :—

$$C_2H_4O_2 \qquad\qquad CH_3OH$$
$$C_2H_4O_2 + Ba{HO \atop HO} = Ba{COOH \atop COOH} + {CHO \atop CH_2HO}$$
$$C_2H_4O_2 \qquad\qquad CH_3OH$$

The upper and lower molecules may be supposed to separate into CO and CH_3OH, the latter separating as methyl alcohol and the former combining with the BaH_2O_2 to form barium formate. In some manner not understood one of hydrogen is by a kind of enzymatic action transferred from one portion to the other of the central dimolecular formaldehyde

$$\frac{CH_2O}{CH_2O} = \frac{CHO}{CH_2HO}$$
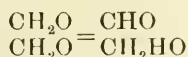
yielding biose or glycollic aldehyde. This would represent a maximum percentage polymerisation to sugar of 33%, and if

tetroses or hexoses were formed directly from biose produced in this way, the percentage polymerization by weight would be the same. If, however, pentoses and hexoses were formed by the direct linking of formaldehyde to the glycollic aldehyde, without further production of formates and methyl alcohol, the polymerisation ratio for pentose would be 9 : 5 (45%), and for glucose would be 10 : 6 (60%). If a dissaccharide were produced, the maximum ratio would be 16 : 12, i.e., 75%.

A monovalent alkali such as sodium hydrate can react with single molecules of $C_2H_4O_2$, producing sodium formate and methyl alcohol, and will only produce a biose when 2 of sodium hydrate react with 2 of $C_2H_4O_2$, with a third molecule interpolated. The chance for this grouping is not more than half what it is in the case of a divalent alkali, where a single molecule reacts with not less than 2 molecules of $C_2H_4O_2$.

Methods.—The same result is not produced when the liquids are mixed cold, and then heated, as when the sodium hydrate is run into the boiling liquid. Thus 250 c.c. of water, with 5 c.c. of 10% calcium formate and 4 c.c. of 25.2% formaldehyde, after raising to the boiling point required, 7.2 c.c. of 3.5% NaHO to complete the reaction. If mixed cold with 7 c.c. of sodium hydrate, on raising to the boiling point a further addition of 0.4 c.c. of NaHO was required to complete the reaction. If mixed cold with 7 c.c. NaHO, and kept for 15 days at 15° C., on raising to the boiling point, the addition of a further 1.2 c.c. of NaHO is required to complete the reaction, and remove all CH_2O. Hence at low temperatures more formate is produced and less formaldehyde is polymerised to sugar, so that more soda is required to remove all the formaldehyde.

In carrying out estimations, a preliminary test was in each case carried out in an open beaker. The amount of sodium hydrate required was less than the full amount by the amount of CH_2O lost during the boiling. The same amounts of CH_2O, water and calcium formate, were then placed in a flask fitted with a condensing apparatus, so that the condensed steam washed back the escaping formaldehyde. The amount of sodium hydrate previously noted was then run in from a burette fitted to the cork, as rapidly as was possible without causing too violent ebullition.

The yellow tinge which indicates the completion of the reaction appears slowly with very dilute solutions, and the preliminary test must be checked by smell as well as colour. With strong solutions the yellow colour is produced before the reaction is completed, if

the soda is added more rapidly than the formic acid is produced. With a little practice these two sources of error are easily avoided.

A solution containing 250 c.c. of water, 5 c.c. of 10% calcium-formate, and 5 c.c. of 31.5% of formaldehyde required 9.6 c.c. of 3.5% sodium hydrate, and required 25.8 c.c. of soda when no calcium formate was present. If no polymerisation had taken place, then the equation would be—

$$2\ CH_2O + 2NaHO\ =\ CH_3HO + Na\ CO\ OH$$
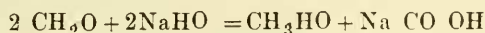
i.e., 60 grams of formaldehyde are required to neutralise 40 grams of sodium hydrate (or 38 grams of calcium hydrate).

3 grams of CH_2O are contained in $\dfrac{3 \times 100}{31.5}$ c.c. of 31.5% solution.

3 grams of NaHO are contained in $\dfrac{2 \times 100}{3.5}$ c.c. of 3.5 solution.

$\therefore$ 1c.c. of 31.5% $CH_2O = 6$ c.c. of 3.5% NaHO.

In the experiment 9.6 c.c. of soda were required, which represents 1.6 c.c. of CH_2O. Hence of the 5 c.c. of formaldehyde used 3.4 c.c. were theoretically polymerised to sugar. In this way, the apparent percentage polymerisation can be calculated under varying conditions, and with various concentrations, as thus :—

Water		c.c. of 10% CaCO$_2$		c.c. of 31.5% OH O		c.c. of 3.5% NaHO required		Per cent. of CH_2O polymerized
250 c.c.	-	5.0	-	5.0	-	9.6 c.c.	-	68
250 c.c.	-	0.0	-	5.0	-	27.8 c.c.	-	8

In addition to sugar, however, small amounts of by-products may appear. Thus perceptible amounts of dihydroxyacetone are produced when formaldehyde is polymerised to sugar by boiling with calcium carbonate.[4] Allowing for this possibility, the percentage polymerisation to sugar is between the theoretical maximum of 75% for the disaccharide and 60% for hexose.

The influence of the concentration of calcium formate present was found by varying the amount added, while keeping the water and formaldehyde constant. Five c.c. of 31.5% CH_2O were added to 250 c.c of calcium formate and water.

The soda first reacts with the calcium formate, forming calcium hydrate and sodium formate. The calcium hydrate reacts with the

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4. H. and A. Culer, Ber.d. D. Bot. Ges. 1905, 39, pp. 36, 39.

Water		c.c. of 10% Ca CO$_2$		c.c. of 3.5% Na HO required		Per cent. of formaldehyde polymerized
250	-	0.0	-	27.7	-	8
250	-	0.1	-	23.9	-	20
250	-	0.2	-	19.8	-	34
249.5	-	0.5	-	17.5	-	42
249	-	1.0	-	14.1	-	54
248	-	2.0	-	11.6	-	62
247.5	-	2.5	-	11.2	-	62
246.5	-	3.5	-	10.1	-	66
245	-	5.0	-	9.8	-	68
240	-	10.0	-	9.8	-	68
235	-	15.0	-	9.8	-	68
230	-	20.0	-	9.7	-	68
210	-	40.0	-	9.7	-	68

formaldehyde, forming calcium formate and polymerising a por-
tion to sugar. No sugar condensation is produced by boiling for-
maldehyde with either calcium or sodium formates.

From the equation $2\ NaHO + Ca(COOH)_2 = CaH_2O_2 + 2\ NaCOOH$
80 grams of soda = 130 grams of calcium formate ‥ 10 c.c. of 3.5%
NaHO = 5.7 c.c. of 10% calcium formate or 9.8 c.c.% of NaHO =
5.5 c.c. of 10% calcium formate. Hence maximum polymerisa-
tion is reached at a point where the soda and calcium formate are
approximately equivalent. After that point an excess of calcium
formate causes no increase in the percentage polymerisation.
When still less calcium formate is present, the amount of soda re-
quired rises, more sodium formate being produced and less sugar.

An addition of 20 c.c. of 10% calcium formate causes an appreci-
able rise of the boiling point, and may be responsible for a slight
loss of formaldehyde either as vapour or in the form of by-products
other than sugar, and not involving any reaction with the calcium
hydrate. Hence the slight decrease in the amount of soda required,
which is in fact easily within the limits of error of the method
used. In a further series of tests, the percentage of calcium for-
mate was kept constant, and the amount of formaldehyde varied.
245 c.c. of water and 5 c.c. of 10% $CaCO_2$ were used in each experi-
ment.

c.c. of 31.5 per cent. CH$_2$O		c.c. of 3.5 per cent. NaHO required		Per cent. of CH$_2$O polymerized
1	-	4.8	-	20
2	-	5.3	-	55
3	-	5.7	-	68
4	-	7.9	-	67.5
5	-	9.8	-	68
5.5	-	14.3	-	56
6	-	18.0	-	50
7	-	29.0	-	31

Apparently an excess of calcium formate interferes with polymerisation, when the formaldehyde is very dilute, while with the strong solutions since the 5 c.c. of 10% calcium formate requires 8.9 c.c. of 3.5% to convert it all into CaH_2O_2, portion of the 5.5, 6 and 7 c.c. of CH_2O has to be neutralised directly by the soda, and hence the percentage polymerization decreases.

Starting with 0.25 c.c. of 10% $CaCO_2$ and 0.5 c.c. of 31.5% CH_2O, and increasing or decreasing each proportionately, the following results were obtained :—

Water		c.c. of 10 per cent. $Ca(COOH)_2$		c.c. of 31.5 per cent. CH_2O		c.c. of 3.5 per cent. NaHO required		Per cent polymerization of CH_2O
249.55 c.c.	-	0.62	-	1.25	-	5.1	-	32
248.75 c.c.	-	1.25	-	2.5	-	6.4	-	56
247.5 c.c.	-	2.5	-	5.0	-	13.0	-	58
245.5 c.c.	-	5.0	-	10.0	-	27.9	-	54
242.5	-	7.5	-	15.0	-	49.0	-	46

On the basis that 1 molecule of CaH_2O_2 reacts with 9 molecules of CH_2O, then 1 c.c. of 10% $Ca(COOH)_2$ represents 0.66 c.c. of 31.5 CH_2O.

Hence the amount of calcium formate present is below that theoretically required, and a large portion of the CH_2O reacts directly with the soda, giving a low percentage polymerisation. Further, two standards were taken, namely, (A) 5 c.c. of 10% $CaCO_2$ to 3 c.c. of 31.5% CH_2O, and (B) 5 c.c. of 10% $CaCO_2$ to c.c. of 31.5% CH_2O. The amounts of each were increased or decreased proportionately to one another in the two sets of tests, A and B, and added to 250 c.c. of water.

A

c.c. of 10 per cent. $Ca(COOH)_2$		c.c. of 31.5 per cent. CH_2O		c.c. of 3.5 per cent. NaHO required		Per cent. polymerization of CH_2O
1.6	-	1.0	-	4.8	-	20
3.3	-	2.0	-	6.2	-	50
5.0	-	3.0	-	6.5	-	63
6.6	-	4.0	-	8.6	-	65
8.2	-	5.0	-	10.1	-	66
9.8	-	6.0	-	13.2	-	63
11.4	-	7.0	-	15.6	-	63
13.1	-	8.0	-	19.2	-	60

B

c.c. of 10 per cent. $Ca(COOH_2)$		c.c. of 31.5 per cent. CH_2O		c.c. of 3.5 per cent. NaHO required		Per cent. polymerization of CH_2O
1.88	-	1.5	-	7.1	-	20
2.5	-	2.0	-	6.4	-	45
3.75	-	3.0	-	7.4	-	60
5.0	-	4.0	-	8.2	-	62
6.25	-	5.0	-	9.4	-	68
7.5	-	6.0	-	11.0	-	70
8.75	-	7.0	-	16.1	-	61'
10.0	-	8.2	-	18.5	-	61

A, contains very nearly the theoretical amount of Ca formate required for the production of pentose sugar (1 mol. Ca formate $= 9$ molecules CH_2O). If any hexose or disaccharide is formed, less calcium formate would be required for optimal polymerisation. The higher polymerization in B indicates that some hexose or di-saccharide is produced. With the intermediate concentrations, the results are very consistent, varying less than 1 % in duplicate tests. At the extremes, however, the results obtained particularly at the lower extreme are apt to vary somewhat, however, carefully the tests are performed.

Evidently, too great an excess of calcium formate interferes slightly with polymerisation at the higher concentrations, whereas in lower concentrations the opposite effect appears to be exercised. The maximum polymerisation is given with concentrations corre-sponding to 0.62% to 0.75% solutions of formaldehyde.

When strong solutions of alkali are used , or when the formalde-hyde is concentrated, portion of the alkali is apt to attack the sugar produced, decreasing the apparent polymerisation.

When calcium formate is present, however, and the soda is added gradually, the percentage polymerisation decreases less rapidly with increasing concentration.

Thus, adding 10% c.c. of 31.5% CH_2O to 50 c.c. of 10% $CaCO_3$ (6.3% CH_2O), 28.8 c.c. of 3.5% Na HO was required to complete the reaction, and an abundance of sugar was formed. In this case 52% of the 6% CH_2O was polymerised. Using a mixture of 50 c.c. of 10% $CaCO_3$, and 20 c.c. of 31.5% CH_2O, and running in 35% NaHO, it is necessary to obtain an approximately accurate result to keep the temperature below boiling point, and to shake vigorously after each addition of soda until the precipitated lime dissolves as formate. Even then the liquid becomes distinctly brown before all the formaldehyde has been removed. The amount of soda averaged 6.6 c.c., and 1 c.c. of CH_2O equalling 0.6 c.c. of soda, the percentage polymerisation was 45.

Polymerisation by other divalent alkaline metals

In the previous paper it was found that the presence of neutral barium, strontium or magnesium salts in boiling formaldehyde, to which caustic soda was added, increased the amount of polymerisa-tion, and decreased the amount of soda required to neutralise the formaldehyde. Barium and strontium were not quite so effective as calcium, and magnesium had comparatively small effect. In these preliminary tests the importance of having a slight excess of

the neutral formate present was not realised, and hence further estimations were carried out in the same manner as for calcium.

It is, however, difficult to obtain exact quantitative determinations owing to the delay in the completion of the reaction after each addition of soda. If the latter is added too rapidly, so that any precipitate forms, this only dissolves very slowly, and any undissolved precipitate represents so much neutralised caustic soda. If, however, the boiling is very prolonged, the liquid turns yellow, while still containing formaldehyde, and when the reaction is completed the liquid appears to contain more by-products other than sugar. At least the liquid from a reaction completed in two hours boiling contained from 5 to 10% more reducing sugar, as determined by the Pavy method, than one completed by six hours' boiling, and the latter required slightly less caustic soda, although all other conditions and quantities were the same.

For these tests it was found best to use a simple type of condensing flask, with the burette passing through the cork, and with an open upright tube 4 ft. long as the condensing column. Of the 500 c.c. of water used 100 c.c. was allowed to trickle slowly down this tube during the two-hour period over which the boiling, and addition of soda, were spread when strontium and barium salts were used. As the soda burette becomes slightly warmed during the boiling, its final reading must be checked after it has cooled to the original temperature.

Strontium.—Crystallised strontium formate was used as a 10% solution. The proportions used were 20 c.c. of strontium formate, 500 c.c. water, and 70 c.c. of 31.5 formaldehyde. The amounts of 3.5% sodium hydrate required varied from 20.8 c.c. to 21.2, representing an apparent polymerisation of formaldehyde of 65%.

Barium.—In the presence of barium formate, using similar quantities, the reaction was slighly more rapid. The amounts of soda required to neutralise all the formaldehyde varied from 20.4 to 20.9, representing a percentage polymerisation of formaldehyde of 65 to 66%.

Magnesium.—Owing to the highly insoluble character of the hydrate, its polymerising action is extremely slow, and quantitative estimations are difficult to obtain. A preliminary estimation was made, using an excess of the hydrate precipitated in the liquid by caustic soda. In this case the only advantage of using caustic soda is that the hydrate is precipitated in a more bulky and flocculent form than if the dry hydrate is used. From the amount

of magnesium hydrate, remaining after all the fomaldehyde had
been polymerised, the approximate amount required was esti-
mated.

Using these proportions more exact estimations were made.   The
condensing flask was provided with a condensing tube 4 ft. long,
which was sealed at the upper end as soon as the liquid had been
brought to boiling point, and allowed to blow out to a thin safety
bulb.   The liquid was then kept just at the boiling point for several
days.   The liquid became brown before the end of each experi-
ment.

In the presence of magnesium formate, 500 c.c. of water and
10 c.c. of 31.5% formaldehyde, after the addition of 23 c.c. of
3.5% sodium hydrate, a small amount of a white insoluble solid still
remained after several days.   This was not $Mg\ H_2O_2$, and was
insoluble in dilute acid, the liquid was faintly acid, and still con-
tained a small amount of CH_2O.

Using 750 c.c. of water, 15 c.c. of 31.5% CH_2O, a slight excess
of magnesium formate and 40 c.c. of 3.5% NaHO, all the formal-
dehyde was removed, after boiling for 22 hours, the liquid was
faintly acid, and contained a small amount of white solid, incon-
spicuous when suspended, but not consisting of $Mg\ H_2O_2$.   This
represents a percentage polymerisation of 58.   A further test gave
a polymerisation value of 57.   As a small amount of the magne-
sium hydrate appears to form an insoluble compound, and as
during prolonged boiling a trace of the formaldehyde is oxidised
directly to formic acid, which represents a further direct removal
of magnesium hydrate without producing any polymerisation, the
polymerisation value of 57 to 58 for the divalent Mg corresponds
fairly well with that of 65-68 for the divalent Ca. Sr, and con-
trasts sharply with the values for the monovalent K and Na of 8 to
14%.

Potassium.—On the basis of the conclusions given above, that
the relative efficiency of calcium and sodium as polymerising
agents depends upon the former being divalent, and the later
monovalent, we should expect to find equivalent solutions of the
monovalent metals, sodium and potassium, exercising a very
much inferior polymerising action, and, that in the presence of
calcium formate it should be a matter of indifference whether
sodium hydrate or an equi-molecular solution of potassium hydrate
was used to bring about polymerisation.

As a matter of fact the correspondence is even more exact than

might have been expected. Thus, using 250 c.c. of water to the proportions given the following were the results :—

c.c. of 10 per cent. calcium formate		c.c. of 31.5 per cent. CH_2O		c.c. of 3.5 per cent. NaHO required		Per cent. polymerization
10.0	-	5	-	9.8	-	68
0.0	-	5	-	27.7	-	8
0.0	-	4	-	22.6	-	6
				c.c. of 4.9 per cent. KHO required		
10.0	-	5	-	9.6	-	68
0.0	-	5	-	26.1	-	14
0.0	-	4	-	20.9	-	12

Non-reducing sugar.

In order to determine whether any non-reducing sugar was formed, to 50 c.c. of calcium sugar concentrated to a thick syrup, BaH_2O_2 solution was added. A small amount of white precipitate was formed. This was filtered, washed, and treated with CO_2. The filtrate contained a non-reducing sugar, giving reduction after boiling with a drop of H_2SO_4, and pink with resorcin and HCl., but no reaction with phenylhydrazin. Hence a small amount of disaccharide resembling cane sugar is formed, but the percentage is much less than 1%, and is greater if the boiling is prolonged during the production of sugar.

In sugar synthesis by Ba and Sr, a small amount of ppt. always forms, which does not dissolve even if boiled with excess of CH_2O. It yields sugar after treatment with CO_2, and is apparently a compound of a disaccharide with BaH_2O_2, or Sr H_2O_2. The amount is always small if the sugar condensation is carried out under proper conditions.

Fischer has shown that in the presence of acids condensation of disaccharides from mono-saccharides, particularly from levulose, is possible, and it seems probable that any disaccharides formed are not produced by directly polymerisation from CH_2O, but indirectly from the monosaccharides. Hence their appearance would not necessarily increase the apparent polymerising action of the alkali.

Reducing power of sugar syrup.

Although the synthetic syrup contains a mixture of sugars, it is of some interest to determine its reducing power in glucose equivalents.

The syrups were formed by running 4.9% potassium hydrate into boiling formaldehyde, containing calcium formate.

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	Water		10 per cent. Ca formate		31.5 per cent. CH$_2$O		Amount req. of 4.9 per cent. KHO
A—	750	-	15 c.c.	-	15 c.c.	-	27.6 c.c.
B—	750°	-	25 c.c.	-	15 c.c.	-	29.5 c.c.

10 c.c. of A were diluted to 50 c.c. with 10% NH$_4$HO, and titrated against 50 c.c. of Pavy's solution (8.316 grams copper sulphate per litre).

34.7 c.c. neutralised 50 c.c. of Pavy. There was no increase in the reducing power after boiling with citric acid.

After heating with 1 drop of HCl., 34.5 c.c. reduced 50 c.c. of Pavy
After heating with 5 drops of HCl., 35.4 c.c. =50 of Pavy.
After heating with 10 drops, 44.5 c.c. decolorised 50 c.c. of Pavy.

Hence a trace of non-reducing sugar may be present capable of inversion by HCl, but excess of HCl causes the decomposition of some of the sugar.

Repeating A and B several times, the maximal reducing action obtained was 33.5 c.c. =50 c.c. Pavy =0.025 gram glucose, and, therefore, the total bulk of 805 c.c. of syrup had a total reducing power equivalent to 1.348 gram of glucose. Since 15·c.c. of 51.5% CH$_2$O were used; in terms of glucose this would represent a sugar polymerisation of 29%.

In a test with caustic soda alone, 35% caustic soda was run into boiling 31.5% CH$_2$O. A yellow tinge appeared at once, but to neutralise all the formaldehyde 25 c.c. of 31.5% CH$_2$O required 14.8 c.c. of 35% NaHO. As 14.8 c.c. are equivalent to 23 c.c. of CH$_2$O, this represents a theoretical polymerisation of 8%. The liquid contained reducing sugar equivalent to 0.13 gram of glucose, which represents a polymerisation in terms of glucose of 2%. Owing to the strength of the alkali used, however, much of the sugar formed is caramelised.

The action of alkalies on the polymers of formaldehyde.

The concentrated aqueous solution of CH$_2$O is supposed not only to contain volatile CH$_2$O, but also hydrates such as $CH_2\genfrac{}{}{0pt}{}{-O-H}{-O-H}$, and $(CH_2)_2O(OH)_2$. The latter is a non-volatile polyhydrate which leaves a waxy solid on complete evaporation, supposed to be diformaldehyde, " paraformaldehyde " $(CH_2O)_2$. The better known triformaldehyde or metaformaldehyde $(CH_2O)_3$ is stated to be distinguished from diformaldehyde by its subliming just over 100°C., whereas its M.P. is 171-172°C., and by its insolubility in water, alcohol and ether.

In contact with peroxides of Ba or Sr, and water, polymerised formaldehydes are catalytically changed into the simple form, and much heat evolved.

There appears to be some uncertainty as to the real nature of "paraformaldehyde," and as to how best to obtain it in pure form.

If a saturated solution of formaldehyde is evaporated by rapid boiling to $\frac{1}{5}$ its bulk, or a 30% to $\frac{1}{6}$ its bulk, and then allowed to cool, it sets as a white waxy solid. A solution containing 175 90°C., then giving off water and CH_2O, recondensing as a solution grams of CH_2O yielded 122 grams of this solid. It melts at of CH_2O, or escaping as gases. In a desiccator or in air it slowly loses water and CH_2O; after three weeks in a desiccator, losing 36% of its weight. If heated to just over 100° c.c. it boils, and after all the water has been driven off the residue sets to a harder waxy solid, with a specific gravity slightly greater than the hydrate (1.2). This gives off CH_2O vapour when heated.

Apparently the first solid obtained is the polyhydrate. This is, however, unstable. After two to three weeks in a dessicator, frequently exhausted by a Geryck pump, a considerable loss of water and CH_2O takes place (nearly 40%), and the residue sublimes on heating. The solid lost on the average 0.8% of its weight daily, until 38% has been lost, by which time the daily loss had fallen to 0.2%.

Both the polyhydrate and the "paraformaldehyde," when in mass, remain incompletely dissolved in cold ether, alcohol or water, even after three days, but in hot water or alcohol dissolve rapidly. On cooling the alcoholic solution, a larger proportion of white solid separates out, which blackens and gives a smell of ether, with warm strong H_2SO_4, and decomposes on heating. It is apparently a compound of CH_2O, with alcohol.

In the intermediate condition between hydrate and $C_3H^6O_3$. changes to CH_2O when heated in water to 130°C. Samples of $C_3H_6O_3$ prepared in various ways, were all found to dissolve slowly, after prolonged heating in excess of boiling water, when in the form of a fine powder. Large pieces, however, give for a considerable time the appearance of being insoluble.

In the intermediate condition between hydrate and $C_3H_6O_3$, it dissolves more readily in hot water than $C_3H_6O_3$. melts partially before subliming, and sublimes into oily drops, which set to a white wax on cooling. When conversion is complete the C_3H_6O, sublimes without melting, and deposits as a white solid.
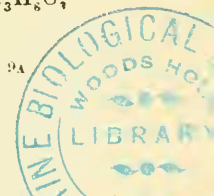
The production of sugar from solids.

If dry $(CH_2O)_3$ is mixed with crystalline Barium hydrate (Ba H_2O_2 8 H_2O) and ground intimately in a mortar, a pasty mass is obtained, smelling of CH_2O. If this is gently warmed at one point a sudden and violent exothermic reaction spreads through the mass, CH_2O, water vapour and methyl alcohol are given off, and the temperature rises to 100° C. or 110° C. if a large mass is used, with an excess of barium hydrate. The resulting brown, gummy residue contains no formaldehyde, but reducing sugar appears.

Similar reactions are given with strontium hydrate, but with dry calcium hydrate the reaction is imperfect. " Paraformaldehyde" and the solid polyhydrate may be used instead of metaformaldehyde. In the latter case the temperature does not rise beyond 100°C., owing to the large escape of steam.

Metaformaldehyde and alkali.

The solid was ground with dry barium hydrate in varying molecular proportions, and the pasty mass weighed out to contain in each case 0.45 gram $(CH_2O)_3$. After warming, the residue was dissolved in warm water, the Barium formate and any excess of Barium hydrate precipitated as sulphate, and the filtrate tested by the Pavy method. Any $(CH_2O)_3$ remaining is filtered off with the Barium sulphate, and if any CH_2O is present, the ammonia used the Pavy method. (Any $(CH_2O)_3$ remaining filtered off with the affect the tests for reducing sugar. Similarly the formic acid is converted into ammonium formate. As a matter of fact the reaction is a very complete one, and with the proper proportion of barium hydrate every trace of formaldehyde is removed.

The following proportions were used :—

A and B. 1 Barium hydrate (0.85 gram) to 1.8 $(CH_2O)_3$ (0.45 gram)
C   1   ,,   ,.   (0.42   ,,) to 3.6 $(CH_2O)_3$ (0.45 gram)
D and E. 1   ,,   ,,   (0.28   ,,) to 5.4 $(CH_2O)_3$ (0.45 gram)

with the following results —

Proportion		Final reaction		Loss of weight after warming	Mass	Reducing equivalent in glucose	
A.	1 : 1.8	Strongly alk.		0.21	Brown	0.075	gram
B.	1 : 1.8	,,	,,	0.23	,,	0 074	,,
C.	1 : 3.6	Less ,,	,,	0.23	Yellow	0.073	,,
D.	1 : 5.4	Weakly alk.		0.17	White or	0.061	,,
E.	1 : 5.4	,,	,,	0.14	pale yellow	0.066	,,.

In B and E the separated ground solids were mixed lightly but thoroughly, and then warmed. In E the mass was mixed and ground with a glass pestle, while the reaction was taking place.

Further investigation showed, however, that to obtain maximum polymerisation, with a minimum loss, quantities totalling not less than 2 grams must be used. Otherwise the reaction is not so complete, and hence the low production of sugar above. The results of three tests are given, the second with a sample of $(CH_2O)_3$ obtained from the Chemistry School, the first and third with samples prepared from a bulk sample supplied by Cuming, Smith's, and purified by sublimation. The proportions used were approximately 4 of $(CH_2O)_3$ to 1 Ba H_2O_2. In all three cases the residue was brown, contained no formaldehyde, and was weakly alkaline.

CH_2O_3		BaH_2O_2		Loss of weight		Reduction equivalent of residue in terms of glucose
1.25 gram	-	0.78 gram	-	0.38 gram	-	0.37 gram
1.25 ,,	-	0.78 ,,	-	0.33 ,,	-	0.39 ,,
2.5 ,,	-	1.56 ,,	-	0.78 ,,	-	0.72 ,,

This represents a polymerisation equivalent in terms of glucose of 30 to 32%. The maximum polymerisation in terms of glucose obtained when using boiling dilute formaldehyde was 29 to 30%. That is, in spite of the loss of formaldehyde vapour, more sugar is obtained from solid metaformaldehyde and crystalline barium hydrate than when the reaction is carried out with dilute solutions in water.

The last experiment (with 2.5 grams) was carried out in a small distilling flask. The distillate weighed 0.45 gram, so that apparently at least $\frac{1}{5}$ of the formaldehyde is lost as vapour. This would increase the actual polymerisation value in terms of glucose to 36%.

Even if an excess of Barium hydrate is used, so that no trace of formaldehyde remains in the residue, the filtered extract gives distinct aldehyde reactions, and hence presumably contains the biose sugar, glycollic aldehyde.

Paraformaldehyde and the polyhydrate.

The former was prepared by melting the latter and heating till water vapour ceased to escape. Similar results were obtained, but the production of sugar was less, and the hydrate gave off more water vapour during the strongly exothermic reaction.

$(CH_2O)_2H_2O$	Alkali		Loss of weight	Glucose equivalent of reducing sugar	Per cent. polymerization in terms of glucose.
2.09 gram	SrH_2O_2	0.8 gram	0.63 gram	0.35	17%
1.53 ,,	$BaH_2O_2 = 1$	,,	0.55 ,,	· 0.34	22%
1.69 ,,	NaHO 0.5	,,	0.74 ,,	0.08	5%
$(CH_2O)_2$					
1.25 ,,	BaH_2O_2 1	,,	0.41 ,,	0.33	26%

In each case the amount of alkali was sufficient to remove all the formaldehyde. When sodium hydrate and the polyhydrate are pounded together, the reaction starts spontaneously, and is very violent. There is a heavy loss of formaldehyde vapour, and much of the sugar is caramelised. For this reason the percentage polymerisation is less than when a boiling dilute solution of formaldehyde is neutralised with dilute sodium hydrate.

If the reaction is started by locally warming several grams of the mixture in a small distilling flask, a large amount of distillate is obtained without applying further heat. This consists in the case of the polyhydrate (and crystalline Ba H_2O_2) of water, methyl alcohol and formaldehyde.

If a slight excess of ·the polydrate is used, the whole of the BaH_2O_2 is converted into barium formate. This can be obtained by dissolving the residue in a little water, and adding an equal bulk of alcohol. A large part of the sugar slowly settles out with some barium formate. On filtering after 48 hours standing, and doubling the bulk in the alcohol, a second ppt., mainly of barium formate, is produced, which can easily be washed and purified.

A point worth noting is that if the finely ground polyhydrate is mixed thoroughly with finely ground crystalline barium hydrate, the mixture smells strongly of formaldehyde, and its temperature falls 15°C. for some time. The temperature then slowly rises, but not appreciably above that of the room. The mixture slowly develops traces of reducing sugar, but does not undergo any complete reaction even after days in contact, until this is started by heating one point of the mixture.

A similar preliminary fall of temperature is shown with di- and tri-molecular formaldehyde. If, however, these are mixed with freshly slaked dry quicklime, or with powdered calcined barium or strontium hydrates, the mixture remains dry, the fall of temperature is hardly noticeable, and on heating the mixture locally the reaction does not spread. Only the parts heated turn brown, and methyl alcohol distils over (yielding methyl iodide with Iodine and red phosphorus). The residue contains an abundance

of reducing sugar, but the reaction is imperfect, and is difficult to complete without overheating portion of the mixture, or volatilising much of the formaldehyde.

It is the presence of water of crystallisation in the crystalline barium hydrate which enables its reaction with solid polymers of formaldehyde to progress, and be completed throughout the whole mixture. Some of this water of crystallisation is liberated by mere contact with solid formaldehyde.

SUMMARY OF RESULTS.

Cold dilute solutions of formaldehyde yield with alkalies, formates and methyl alcohol, sugar polymerisation being inappreciable. The reaction is incomplete after months in contact.

Maximum sugar production is given with boiling liquids, and the reaction is completed almost instantaneously.

The maximum sugar polymerisation varies from 68% (Ca), 66% Ba, 65% Sr. to 58% Mg. for divalent alkalies, and from 14% (K) to 8% (Na) for monovalent alkalies. The high polymerisation value (68%) estimated from the amount of alkali required for neutralisation indicates either that the pentoses and hexoses are produced directly, or that glycollic aldehyde is produced by the reaction yielding formates, and 3 or 4 of formaldehyde added to it without further decomposition of formaldehyde. This is also indicated by the appearance of pentoses. Polymerisation of biose would yield tetroses or hexoses, but not pentoses.

The greatly increased polymerisation when soda is run into a solution of formaldehyde containing calcium formate is merely due to the fact that calcium hydrate becomes the polymerising agent, and as a divalent metal exercises a greater polymerising action. There is no evidence of any katalytic action, as was formerly supposed.

In terms of glucose, the reducing sugars produced represented a polymerisation of 29% for calcium, and 2% for sodium. Apparently the sugars have half the reducing power of glucose.

The solid polymers of formaldehyde yield sugar readily, and abundantly, when in contact with solid alkalies. The most complete reaction is shown with the powdered crystalline hydrates of Ba and Sr. A feeble endothermic reaction precedes the violent exothermic one. The production of sugar is greater than with solutions, the polymerisation equivalent in terms of glucose being 30-32%.

In all cases the sugar is a by-product in a reaction, yielding for-

mates and methyl alcohol. The alkali is used up and the amount of sugar formed is proportionate to the amount of alkali consumed. The reaction is, therefore, widely different from an enzymatic one. No mode of enzymatically polymerising formaldehyde to sugar is known, such as might occur in plants.

Conclusions.

The foregoing research was undertaken in order to elucidate certain points of interest to the plant physiologist concerning the possible modes in which plants could synthesize sugar from formaldehyde, which the purely chemical researches available did not appear to answer. It has led me to the conclusion that a production of formaldehyde does not form a stage in the synthesis of sugar by plants, and that it would be a very wasteful, indirect way of producing sugar.

The reasons on which this conclusion are based are as follow :—

(1) In 1908 I showed that when chlorophyll was oxidised in the presence of light, and in the absence of carbon-dioxide, one of its decomposition products was formaldehyde, and that this was the explanation of the appearance of traces of formaldehyde in green leaves exposed to light. This result has been confirmed by Schryver and by Jorgensen and Kidd.* Schryver stated that more formaldehyde was produced when carbon dioxide was present, but as the results of experiments extending now over ten years, there can be no doubt that the process is purely one of photo-chemical oxidation, and is not increased by the presence of CO_2.
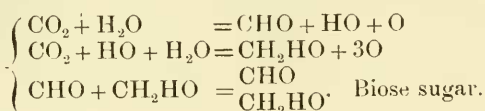
(2) There are strong reasons for concluding that alkalies do not polymerise formaldehyde to sugar, or only to a very slight extent, but instead produce methyl alcohol and formates. Pronounced sugar formation only takes place when the alkali acts on a polymer, such as paraformaldehyde, the polyhydrate, or metaformaldehyde. The production of sugar from a solution of formaldehyde mainly depends on the presence of the polyhydrate in the solution. With cold dilute solutions the production of sugar is almost negligible. For a complete reaction and high polymerisation a temperature of 90°C. to 100°C. is necessary. Even then the polymerisation is only partial, and formates and methyl alcohol are formed in large amount. These are not known to accompany photosynthesis in plants.
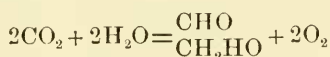
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* Ewart, Proc. Royal Soc. Lond., B 1908, Vol. 80, p. 30 ; Schryver, *ibid.* 1910, 82, p. 226 ; Jörgenson and Kidd, *ibid.* 1917, 89, p. 342.

(3) Every method of polymerising formaldehyde to sugar yields a mixture of sugars, in which pentoses are included, and often form the main yield. Pentoses are not direct products of photosynthesis in plants, but instead hexoses and their 6 or 12 carbon derivatives, starch and polysaccharides.
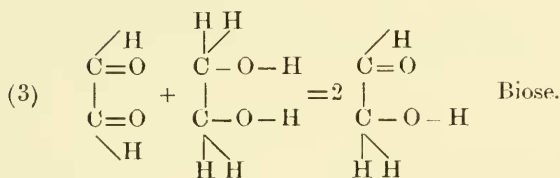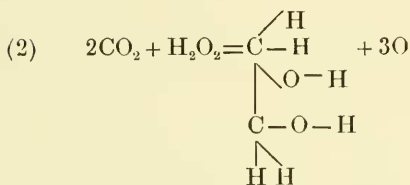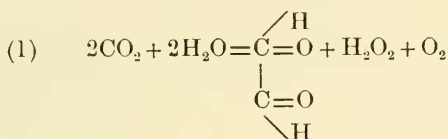
(4) It is as easy for the plant to produce sugar directly as to produce formaldehyde. Thus taking the process in three stages—

$$\begin{cases} CO_2 + H_2O & = CHO + HO + O \\ CO_2 + HO + H_2O = CH_2HO + 3O \\ CHO + CH_2HO & = \dfrac{CHO}{CH_2HO}. \quad \text{Biose sugar.} \end{cases}$$

or in one stage :—

$$2CO_2 + 2H_2O = \frac{CHO}{CH_2HO} + 2O_2$$

The equation could also be represented as in 1, 2, 3.

(1)
$$2CO_2 + 2H_2O = \overset{\diagup H}{\underset{\diagdown H}{C=O}} \;\; \overset{|}{\underset{C=O}{}} + H_2O_2 + O_2$$

(2)
$$2CO_2 + H_2O_2 = \overset{\diagup H}{\underset{\diagdown O-H}{C-H}} \;\; \overset{|}{\underset{H\ H}{C-O-H}} + 3O$$

(3)
$$\overset{\diagup H}{\underset{\diagdown H}{C=O}}\,\overset{|}{\underset{C=O}{}} + \overset{H\ H}{\underset{H\ H}{\underset{|}{C-O-H}}}\,\overset{}{\underset{}{C-O-H}} = 2 \;\overset{\diagup H}{\underset{\diagdown H\ H}{C=O}}\,\overset{|}{\underset{}{C-O-H}} \quad \text{Biose.}$$

(5) This Biose sugar (glycollic aldehyde) is readily polymerised by sodium carbonate to acrose, a hexose sugar.

(6) This mode of producing sugar would be endothermic, as in the plant. The production of sugar from the polymers of formaldehyde involves an exothermic reaction which, under appropriate conditions, is very violent.

(7) Magnesium hydrate has a slower polymerising action on formaldehyde than any other metallic alkali. Since the presence of magnesium in chlorophyll is hardly accidental, its relations to glycollic aldehyde when it is in organic combination merit future

investigation. For it to be able to act as a polymeriser in the plant, it must act in ferment fashion without itself being altered or brought permanently into different combination. That is the polymerising action must differ widely from that of alkalies on formaldehyde and its polymers.

(8) If photosynthesis involves an actual combination of chlorophyll and carbon dioxide, which combination is distintegrated by light into chlorophyll and carbohydrate, hexoses would be formed as readily directly as through the intervention of biose and the chlorophyll would act as a lytase or carboxidase enzyme.* Its mode of action in producing glycollic aldehyde would also be that of an enzyme.

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* Proc. Royal Soc. of Vict. 1918, Vol. xxx. p. 208.